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| 14. ABSTRACT A primary goal of the research is optimization of the intercalation/exfoliation of graphite. We have tested various starting graphites and found that low cost Natural Graphite from Cornerstone is ideal since intercalation of potassium to form the first stage intercalation compound KC8 is complete upon heatings at 2000C. We have also optimized the synthesis of KC8 and increased the reaction to a 100 gram scale using a one liter round-bottom reaction vessel with Teflon stopcock. | | | | | |
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NANOCOMPOSITES FOR ENHANCED STRUCTURAL INTEGRITY

AFOSR GRANT F49620-02-1-0414

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I. Progress in Synthesis of Graphite Nanoplatelets

A primary goal of the research is optimization of the intercalation/exfoliation of graphite. We have tested various starting graphites and found that low cost Natural Graphite from Cornerstone is ideal since intercalation of potassium to form the first stage intercalation compound KC_8 is complete upon heating at 200°C . We have also optimized the synthesis of KC_8 and increased the reaction to a 100 gram scale using a one liter round-bottom reaction vessel with Teflon stopcock.

Exfoliation of KC_8 with ethanol produces graphite nanoplatelets (GNP). We have experimented with various exfoliation procedures and found that multiple filtrations aids in removing the potassium metal. To remove all potassium metal, KC_8 is exfoliated using ethanol and then sonicated (80 Watt bath sonicator) and filtered several times until a neutral pH is achieved. It is believed that weak sonication, which induces removal of the potassium, promotes separation of the graphite layers. Scanning electron microscopy (SEM) images reveal that the graphite sheets are expanded to an "accordion" structure (Figure 1).

Reduction of particle size is of prime importance. Ball milling both before and after intercalation was carried out to reduce the particle dimensions. Milling of the intercalation compound KC_8 , prior to exfoliation, was found to yield smaller sized platelets as determined by SEM.

Following removal of the bulk solvent, further drying of the graphite nanoplatelets was explored. Ethanol exfoliated GNP powder was supercritically dried (in collaboration with Dr. John Starkovich at Northrup Grumman) using the gas/liquid phase of supercritical ethanol. Freeze drying of water exfoliated GNP powder (also in collaboration with Dr. Starkovich) was carried out to remove all remaining water from the sample. For both the supercritically and freeze dried samples, thermal gravimetric analysis (TGA) revealed that the graphite nanoplatelets were completely dry since no solvent loss was observed. A third technique of drying using microwaves was found to work exceptionally well. A sample of ethanol soaked GNP was microwaved to achieve further exfoliation. Upon addition of microwaves, the ethanol boils rapidly thereby expanding the graphite sheets to

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a greater degree. SEM images of the microwaved GNP demonstrated ultra thin graphite nanoplatelets with an average thickness of 50 nm.

Obtaining stable, uniform dispersions of the platelets within the polymer matrix is crucial. To aid in mixing of the graphite nanoplatelets in the polymer solution, various surfactants have been tested. Exfoliation of the GNP using a solution of ethanol and surfactant was performed. Carboxymethylcellulose (CMC) and sodium dodecylsulfate (SDS) were used to help disperse the platelets in the epoxy matrix.



Figure 1. Scanning electron micrograph of graphite nanoplatelets showing the expanded structure of the graphite layers as a result of the intercalation/exfoliation process.

II. Electrospinning of GNP/PAN Nanofiber Composites

Graphite sheets are attractive as a reinforcement material due to their superior stiffness and high strength per unit weight. Nanofiber composites of graphite nanoplatelets (GNP) and polyacrylonitrile (PAN) were synthesized and tested for their mechanical and thermal properties. The composite solutions were prepared by dissolving 7 weight percent PAN in dimethylformamide (DMF) and then adding between 1 to 4 weight percent of GNP. The composite solutions were then sonicated to insure dispersion of the platelets in the polymer matrix. The nanoplatelets were extruded into a PAN matrix by the electrospinning process to create ultrafine GNP/PAN composite fibrils, thus providing a convenient means for the distribution of the GNP.

Scanning electron microscopy (SEM) characterization demonstrated uniform GNP/PAN nanofibers with an average diameter of 200 nm. Transmission electron microscopy (TEM) in selected area electron diffraction (SAED) mode revealed the presence of GNP in the PAN fibril matrix since the hexagonal diffraction pattern of graphite is observed and PAN is amorphous (Figure 2). Thermal gravimetric analysis (TGA) of the GNP/PAN composite nanofibrils showed an increase in thermal stability with increasing weight percent of GNP. The mechanical properties of the composite fibrils were then examined

using an atomic force microscopy (AFM) nanohardness technique.¹ Young's modulus of the 1-4 wt % GNP/PAN composite fibrils were measured and plotted. A five-fold increase in reinforcement effect was observed. The increase in Young's modulus, with increasing weight percent GNP, was found to be greater than calculated by the rule of mixture where $E_{\text{mixture}} = E_{\text{PAN}}(\% \text{PAN}) + E_{\text{GNP}}(\% \text{GNP})$.^{2,3}

With an aspect ratio of over 1000, the GNP provide an efficient means for stress transfer and thus serve as an excellent reinforcement for nanofiber composites. Based on these encouraging results, further investigations are being carried out with other polymer matrices.

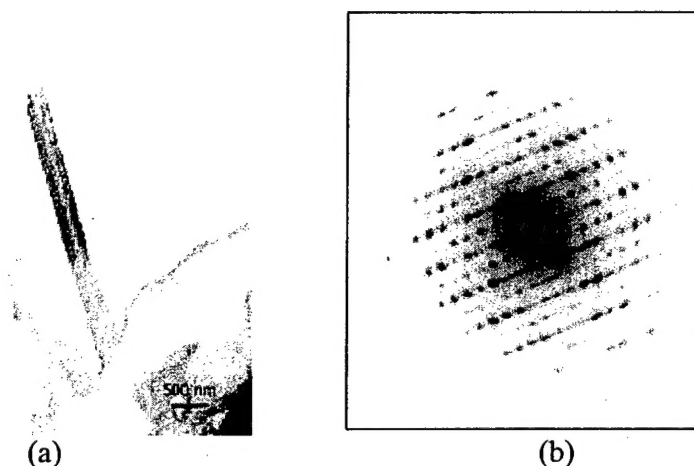


Figure 2. (a) Dark field TEM image of a 1 wt. % GNP/PAN nanofiber composite. (b) The selected area electron diffraction pattern of GNP incorporated within the PAN nanofiber.

III. *In Situ* Polymerization

One approach that we have been using to improve the dispersion and separation of graphitic sheets within the polymer matrix is through *in situ* polymerization. Following the work of Shioyama,⁴ we have been experimenting with polymerizing styrene monomers within potassium intercalated graphite layers. Starting with the first stage intercalation compound, KC_8 , styrene vapor is absorbed and polymerization is anionically initiated by the negatively charged graphite sheets. Over time, a large volume expansion is observed as more and more styrene is added to this "living polymer" and the carbon sheets are forced further apart (Figure 3). The process ends when the styrene source is exhausted. This experiment has also been done with a vinyl ester resin, commercial name Derakane, which is comprised of 30 wt. % styrene. Preliminary results show that *in situ* polymerization can be initiated with this resin as well. However, the high viscosity of Derakane makes vapor transport to the KC_8 difficult. Microscopy work is under way to look at how well the sheets are separated and dispersed within the

composite. One advantage of a thermoplastic polystyrene composite is that it can be redissolved with various organic solvents such as benzene, tetrahydrofuran, and carbon tetrachloride. Redissolving the polystyrene composite may provide a route towards individual graphene sheets that could later be added to other commercially important thermoset polymers.

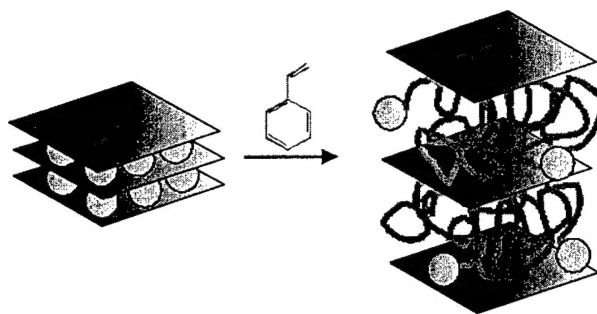


Figure 3. The first stage intercalation compound, KC_8 , (gold = K^+) is exposed to styrene vapor and *in situ* polymerization is anionically initiated, forcing the graphite sheets further apart.

IV. Carbon Nanoscrolls

We recently reported the synthesis of carbon nanoscrolls by intercalation/exfoliation of graphite, following by high energy sonication.⁵ The graphitic sheets minimize their free surface energy by scrolling onto themselves when agitated in aqueous solvent (Figure 4(a)). The carbon nanoscrolls are analogous to multi-walled carbon nanotubes, however without the end caps. We have found that it is only the thinnest sheets of graphite (on average 40 ± 15 layers) that will curl upon themselves. Transmission electron microscopy shows an 80 % yield of carbon nanoscrolls (Figure 4(b)), yet the bulk of the exfoliated graphite has not been reduced down to nearly individual sheets.

Current techniques that we are employing to decrease sheet thickness, and thus increase the overall carbon nanoscroll yield, is through super-critical drying, freeze-drying, *in situ* polymerization, and reducing the initial platelet size in the *ab* direction via mechanical grinding. Recent reports demonstrate improved mechanical properties for electrospun composites with aligned single walled carbon nanotubes.⁶ Our aim is to increase the carbon nanoscroll yield via the methods mentioned above, so that electrospun composites can be spun and their resulting mechanical properties tested. Carbon nanoscrolls would provide an affordable and scalable alternative to the currently expensive purified single walled carbon nanotubes.

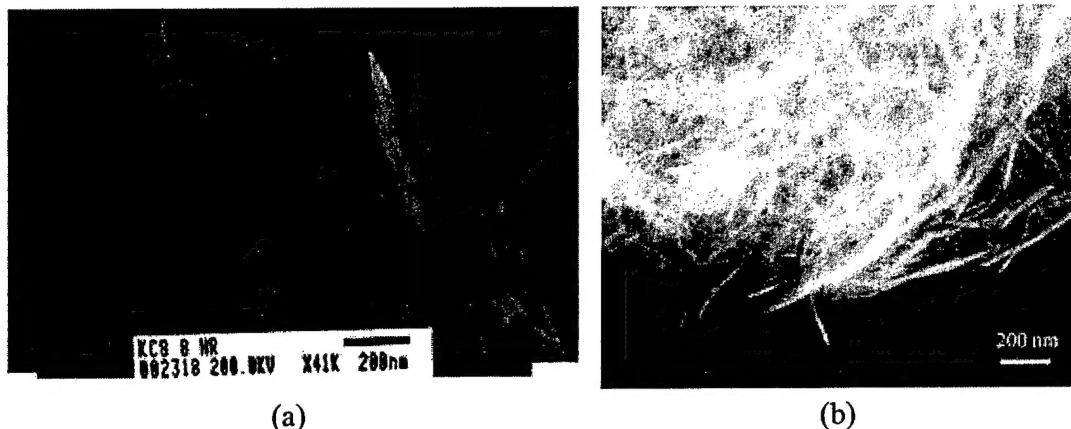


Figure 4. (a) Transmission electron micrograph showing a thin sheet of graphite scrolling onto itself. The lighter web pattern in the background is the lacey carbon grid support. (b) Representative image of the bulk of the carbon nanoscroll sample, as observed by transmission electron microscopy. The lighter web pattern in the background is the lacey carbon grid support.

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